FROM SMALL TO LARGE MOLECULE SUBSTRATES IN OSCILLATORY CARBONYLATION

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ABSTRACT

Over the past two decades the oscillatory nature of the PdI_2-catalysed oxidative carbonylation of phenylacetylene has been experimentally studied and reproducible oscillations in pH were reported. Oscillatory behaviour has been reported over the temperature range 0-40 °C under batch or semi-batch conditions. Recently, oscillatory palladium-catalysed carbonylation has been achieved using mono alkyne-terminated poly(ethylene glycol) methyl ether at 20 °C demonstrating that alkyne-terminated macromolecules are also suitable substrates. In this work, studies of both oscillatory systems (phenylacetylene and mono alkyne-terminated poly(ethylene glycol) methyl ether) conducted in a 1 litre automated reactor system are reported.

INTRODUCTION

Oxidative carbonylation reactions are important C-C bond forming reactions that generate a number of products depending on the substrates, catalyst and reaction conditions [1-7]. Using a PdI_2-KI catalyst with alkynes under mild conditions good catalytic efficiencies have been achieved leading to a mixture of dicarbonylation products [8]. Importantly, when phenylacetylene (PhAc) was used as the substrate in methanol, oscillations in pH, redox potential, gas uptake (CO and O_2), reaction heat (Q_r) and turbidity were discovered [9-17]. The observed duration of oscillations varied from several hours [9-13] to several days [15, 16], with reaction temperatures ranging from 0 to 40 °C [15, 16]. The magnitude of heat released is significant and based on the initial charge of PhAc alone up to 10.37 $kJmol^{-1}$ per oscillation was recorded. Oscillations in Q_r were exothermic and no corresponding endotherm was observed. Heat release was in phase with the pH fall and decreased as the pH increased indicating the formation of reaction products in a stepwise manner [12]. While the PhAc oscillatory system was initially of interest as a novel organic pH oscillator operating in a stirred batch

reactor system, the recent discovery of oscillatory alkyne-terminated polymeric systems has opened new avenues and unambiguously indicated opportunities for the discovery of other alkyne-based oscillatory reaction systems. Oscillatory palladium-catalysed carbonylation has been reported using mono alkyne-terminated poly(ethylene glycol) methyl ether at 20 °C [18]. Reproducible, synchronised oscillations in pH and solution turbidity have been recorded over several days [18]. In this study both PhAc and mono alkyne-terminated poly(ethylene glycol) methyl ether were experimentally studied on the same scale using a 1 litre automated reactor. The initial conditions used to achieve oscillatory behaviour as well as trends in the recorded pH oscillations are discussed.

EXPERIMENTAL

The study was conducted in an HEL Simular reaction calorimeter. The setup consists of a 1 L double-jacketed glass reactor. Reactor temperature is monitored by a Pt100 temperature probe while internal heating is provided by a 150 W internal heater. The oil jacket temperature is controlled by a Julabo FP50-HD circulator. The reactor is fitted with a combined pH electrode. Stirring is provided by an overhead pitched blade impeller. The reactor has two mass flow controllers which dose air and CO. The installed WinISO software allows the HEL Simular to run unaided once it is set up. All data are automatically saved via the HEL IQ data logging software. The PhAc experiment was conducted in methanol (450 mL) heated to 20 °C while stirring at 250 rpm. The palladium(II) iodide (2.64×10^{-3} moldm^{-3}) and KI (0.494 moldm^{-3}) were added and, after approximately 50 min, purging with CO and air at 50 mLmin^{-1} commenced. PhAc (0.124 moldm^{-3}) was added to the reactor 20 min after purging began. The mono alkyne-terminated poly(ethylene glycol) 2000 Da (PEGA2000) derivative was synthesised according to literature procedures [19-21]. When PEGA2000 was used, instead of PhAc, the initial substrate concentration was 1.52×10^{-3} moldm^{-3} in 450 mL of methanol. The concentrations of PdI_2 and KI were 2.9×10^{-5} and 5.7×10^{-3} moldm^{-3} respectively. Both experiments were conducted using the power compensation mode of the reaction calorimeter. Temperature was maintained at 20 °C and pH was recorded throughout with additional methanol added as necessary to compensate for evaporative loss of the solvent.

RESULTS AND DISCUSSION

The pH recorded employing PhAc is shown in Figure 1 while the pH recorded in the oscillatory PEGA2000 run is given in Figure 2. A summary of trends observed in these two experiments is given in Table 1.

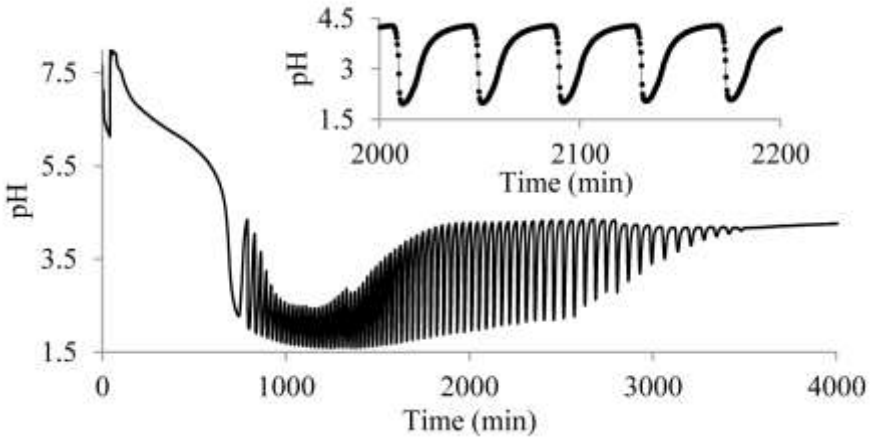

Figure 1. The pH in PhAc carbonylation at 20 °C. [PhAc] = 0.124 moldm^{-3}; [PdI_2] = 2.64x10^{-3} moldm^{-3}; [KI] = 0.494 moldm^{-3}; CO = 50 mLmin^{-1}; Air = 50 mLmin^{-1}.

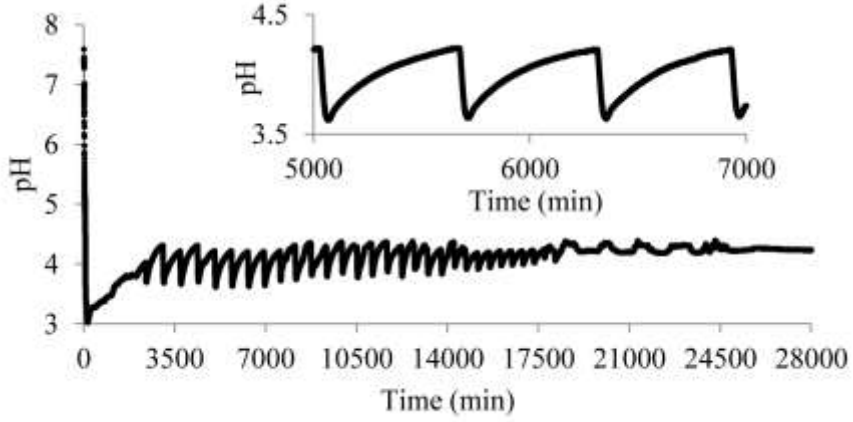

Figure 2. The pH in PEGA2000 carbonylation at 20 °C. [PEGA2000] = 1.52x10^{-3} moldm^{-3}; [PdI_2] = 2.9x10^{-5} moldm^{-3}; [KI] = 5.7x10^{-3} moldm^{-3}; CO = 50 mLmin^{-1}; Air = 50 mLmin^{-1}.

While long lasting oscillations were achieved under semi-batch conditions in both experiments (Figures 1 and 2), pH oscillations recorded when

PEGA2000 was employed as substrate lasted approximately 16 days which is more than eight times longer than when PhAc was used (Table 1). Importantly, this was achieved with an approximately 82 times lower initial concentration of substrate and 91 times lower concentration of catalyst.

Table 1. A summary of trends in the pH oscillations in the PhAc and PEGA2000 reactions at 20 °C.

Run	PhAc	PEGA2000
pH at onset of oscillations	2.27	3.74
Onset time of oscillations (min)	744	2390
Duration of oscillations (min)	2737	22610
Max amplitude (pH units)	2.35	0.6
Max period (min)	71	677

The transition to polymeric substrate in this oscillatory reaction system likely led to a reduction in the carbonylation reaction rate. This postulation is supported by the observed increase in period of oscillations which is in agreement with the previously proposed key step responsible for product formation (Eq.1) the rate of which is anticipated to decrease as the size of molecule increases [16].

$$\text{Alkyne} + \text{PdI}_2 + 2\text{CH}_3\text{OH} + 2\text{CO} \xrightarrow{\text{HI}} \text{Products} + \text{Pd} + 2\text{HI} \qquad \text{Eq.1}$$

The reduction in the reaction rate in the PEGA2000 system is also likely to be responsible for the significantly longer induction period prior to the onset of oscillations (Table 1). At the same time, the lower PdI_2 concentration used in the PEGA2000 experiment will lead to smaller reaction cycles resulting in a reduced amplitude of oscillations.

CONCLUSION

This work shows two oscillatory carbonylation systems, PhAc and PEGA2000, studied at the same scale. The transition from small molecule (PhAc) to polymeric substrate (PEGA2000) enabled a significant reduction in initial concentration of both substrate and catalyst needed for the oscillations to occur. Furthermore, the polymeric substrate significantly affected the rates involved in this oscillatory process prolonging the period as well as the duration of oscillations (approximately 16 days). At the same time, the reduced catalyst concentration reduced the amplitude of the oscillations.

Oscillatory alkyne-functionalised polymeric substrate carbonylation reactions and the additional degrees of freedom macromolecules bring (e.g. chain length and multifunctionality) open new avenues in the area of nonlinear dynamics and has the potential to enable the transition from liquid based oscillators to solid state oscillatory systems.

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